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INFLUENCE OF ORGANIC ADDITIVES ON MORPHOLOGY AND PURITY OF CATHODIC SILVER

WPŁYW DODATKÓW ORGANICZNYCH NA MORFOLOGIĘ I CZYSTOŚĆ SREBRA KATODOWEGO

Influence of some organic additives on morphology and purity of cathodic silver was investigated. Silver was deposited from acidic nitrate solutions doped with Cu^{2+} and Pb^{2+} ions. Bright silver powder was deposited from bath without any additives. The powder poorly adhered to substrate and characterized with the hollow grains. Thiourea addition to the bath resulted in silver sulphide precipitation making silver electrodeposition impossible. Silver deposited both as compact metal and as powder in the presence of tartaric acid, while from the bath with sodium lauryl sulphate addition, silver deposited only as the powder. The morphology of powders depended strongly on additive concentration in the electrolyte. The silver deposits were contaminated with copper and lead, but their contents were depended on the bath composition.

Określono wpływ wybranych dodatków organicznych na morfologię i czystość osadów katodowych srebra. Srebro otrzymywano na drodze elektrolizy kwaśnych roztworów azotanowych dotowanych jonami Cu^{2+} i Pb^{2+}. Srebro otrzymane kąpieli bez dodatków organicznych ma postać błyszczącego proszku, luźno związanego z podkładką katodową, ziarna proszku nie stanowią litych brył. Dodatek tiomocznika do kąpieli prowadzi do wytrącania się siarczku srebra, co uniemożliwia prowadzenie elektrolizy. W obecności kwasu winowego srebro wydziela się zarówno w postaci litej, jak i proszku. Laurylosiarczan sodu prowadzi do tworzenia się proszkowego osadu katodowego. Morfologia proszku srebra uzależniona jest od stężenia związku organicznego w elektrolicie. Uzyskano osady srebra zanieczyszczone miedzią i ołowiem, przy czym zawartości obu metali zależą od składu roztworu.

1. Introduction

High purity silver is obtained traditionally by an electrorefining process from nitrate solutions. As anode a Dore metal is usually used. In polish industrial practice [1], the Dore metal contains on average: 99.1–99.5% Ag, 0.3–0.8% Cu and 0.01–0.02% Pb (main constituents). Anode dissolution in the process of the electrolysis leads to gradual increase of copper and lead ions concentrations in the bath and thus to the contamination of the cathodic silver. Under the industrial conditions the final product with min. 99.99% Ag, 10–30 ppm Cu and 2–4 ppm Pb is obtained from the bath containing: 110–130 g/dm^3 Ag^+, 20–30 g/dm^3 Cu^{2+} and 0.2–1 g/dm^3 Pb^{2+}. Mechanism of copper and lead transfer from the anode into the cathodic silver is not well known. Harańczyk and Sędzimir [2] showed three possibilities:

- hydrolysis of copper and lead salts and precipitation of their hydroxides at the stage of washing of silver deposit. However, application of acidified water and subsequently the neutral hot water should eliminate this problem.

- cathodic codeposition of copper and lead with silver. It was proved experimentally, that silver deposits from nitrate solution (100 g/dm^3 Ag^+) at potentials of 0.7–0.8 V (vs NHE). Equilibrium potentials of copper and lead are, respectively: 0.46 V (126 g/dm^3 Cu^{2+}; 80 ppm Cu in the cathodic silver) and 0 V (20 g/dm^3 Pb^{2+}; 15 ppm Pb in the cathodic silver), if copper and lead activity coefficients in silver are assumed to be equal one. These potentials are considerably lower than the value accepted for silver deposition. It indicates no possibility for copper and/or lead codeposition with silver from nitrate solutions. Under the industrial conditions, Cu^{2+} and Pb^{2+} concentrations in the bath are much lower and it further decreases probability of their codeposition.

- occlusion of electrolyte traces in the cathodic deposit. It was estimated that 1 g of silver contains about $6 \cdot 10^{-4}$ cm^3 of solution closed in tight micro-

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cavities. It seems that the change in the deposit morphology would inhibit this process.

Silver electrodeposits from nitrate solutions in form of independent crystals and dendrites. It was shown that some compounds used in the silver plating can modify cathodic process giving in some cases compact silver deposits. Thiourea [3], tartaric acid [4, 5] and phosphate ions [6, 7] were used most often.

The aim of this work was to estimate the applicability of several additives in the silver electrorefining. It would be interesting to find out if the additives can decrease copper and lead contents in the cathodic silver. In preliminary considerations phosphate ions were eliminated, since Ag_3PO_4 precipitation was expected (since $L_{Ag_3PO_4} = 1,8 \cdot 10^{-18}$, for 120 g/dm^3 Ag$^+$ (1.1 M) in the bath, precipitation would occur at only 10^{-16} g/dm^3 H_3PO_4 (10^{-18} M)).

2. Experimental

The silver deposition was carried out in acidified silver nitrate solutions doped with copper and lead nitrates. Three additives were used: thiourea (TU), tartaric acid L(+) (TA) and sodium lauryl sulphate (SLS). The concentrations of each component in the baths are presented in the Table 1. pH of electrolytes was 1.8. The electrolysis was performed in cuboid PVC vessel containing 1 dm^3 of the solution. Square stainless steel plate (3cm × 3cm × 0.1cm) as cathode substrate and two silver anodes (3cm × 3cm × 1cm) were used. The

electrodes were hung vertically in the electrolyser. The anodes were placed symmetrically on both sides of the centrally located cathode. Prior to each experiment the cathode was cleaned with abrasive papers. Before and after measurement all electrodes were washed in distilled water, alcohol, dried and then weighted. Peristaltic pump forced the circulation rate of 24 dm^3/h of the bath agitation. All measurements were performed for 1h under galvanostatic conditions at current density of 1050 A/m^2 (calculated to the geometrical area of the cathode). Temperature of the electrolyte was 55 ± 0.2°C.

During electrolysis silver was removed mechanically from the cathode substrate in 5 s periods. After measurement electrolyte was filtered and cathodic deposit was washed in two stages: with the warm (50°C) acidified (with HNO$_3$, pH 3) water and then with warm, neutral distilled water. Silver powder was dried in 100°C to the constant mass. Samples of cathodic silver were dissolved in hot HNO$_3$ (1:1) as well as they were examined by scanning electron microscopy (Stereoscan 120, Cambridge Instruments).

In the course of electrolysis, three samples of the solution were taken and the concentrations of Ag$^+$, Cu^{2+} and Pb^{2+} were determined. Silver content in the bath was determined by conductometric titration with 0.1 M NaCl, while copper and lead concentrations by AAS method (Perkin Elmer Atomic Absorption Spectrometer 3110). Copper and lead in the cathodic deposit were determined by ICP method (Perkin Elmer ICP AES "Plasma 40"). Accuracy of all analysis's was ± 3 ppm for copper and ± 2 ppm for lead.

The composition of baths

Bath component	Bath "NO"	Bath "TU"	Bath "TA"	Bath "SLS"
	g/dm^3			
as nitrates:				
Ag$^+$	120.8	120.8	120.8	120.8
Cu^{2+}	28.3	28.3	28.3	28.3
Pb^{2+}	0.8	0.8	0.8	0.8
thiourea	–	10.0	–	–
tartaric acid L(+)	–	–	2.2; 1.1; 0.6	–
sodium lauryl sulphate	–	–	–	0.08; 0.02

Adsorption of copper and lead ions on the silver powders was tested. Samples of the metallic silver (about 1g) were immersed for 12 hours at room temperature in the solutions containing 0,5 g/dm^3 and 0,05 g/dm^3 Cu^{2+} or Pb^{2+} or both Cu^{2+} and Pb^{2+}. Concentrations of Cu^{2+} and Pb^{2+} in the solutions were determined by AAS method.

3. Results and discussion

3.1. No additives

At first, the electrodeposition of silver from the electrolyte without any organic additives (bath "NO")

was investigated. Silver deposited as bright powder. It was adhering poorly to the substrate surface and could be easily mechanically removed. The powder consisted of two fractions: fine-grained powder and dendrites.
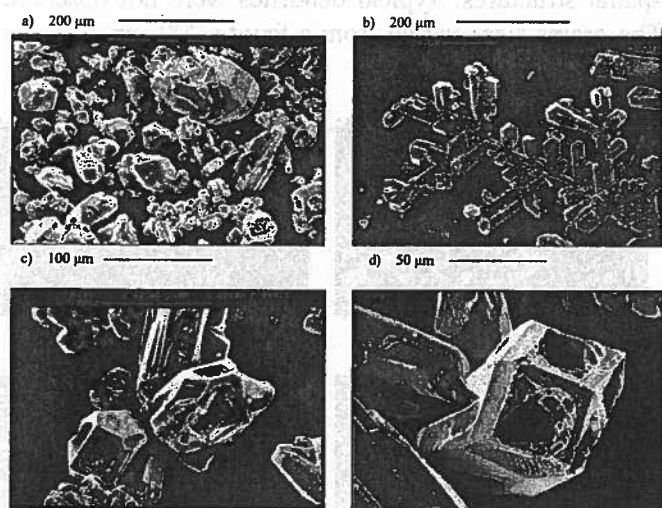

Fig. 1. The morphology of the silver powder deposited from the bath without organic additives

SEM analysis of the fine-grained fraction showed independent silver polyhedrons (Fig. 1a). Their external faces were flat surfaces. Most of the crystals were in the form of agglomerates. Hence, the silver grains showed different sizes: from 20 μm to 200 μm. The second fraction of the powder consisted of the dendrites with characteristic branched structure (Fig. 1b). They were rather long (even over 1000 μm).

The silver crystallites were not monolithic. It seemed that only crystal faces grew up, while interior of the grains remained hollow (Fig. 1c-d). It would favor occlusion of the electrolyte in the cathodic deposit. The contents of the copper and lead in the cathodic silver were 20 ppm and 8 ppm, respectively. According to data obtained for copper it was evaluated that the electrolyte occlusions would be equal $7 \cdot 10^{-4}$ cm^3 per one gram of the silver deposited. Similar calculations were made by Harańczyk and Sędzimir [2] and the same results were obtained. Analogous calculations made up on data for lead gave values of one order of magnitude higher than for copper. It is obvious since Cu:Pb ratio in the cathodic deposit is lower than as in the electrolyte. This effect was detected both in industrial practice as well as in the laboratory research [9]. This phenomenon can be explained by preferential adsorption of Pb^{2+} than Cu^{2+} on the metallic silver. The tests showed that adsorption of Pb^{2+} ions was 0,08 ppm/g Ag and 8 ppm/g Ag for Pb^{2+} concentrations 0,05 g/dm^3 and 0,5 g/dm^3 respectively. Cu^{2+} adsorption was not observed.

Similar morphology of the cathodic silver was observed by Popov et al. [8]. They investigated the silver deposition on silver substrates from pure nitrate bath (53,5 g/dm^3 Ag$^+$ + 31,5 g/dm^3 HNO$_3$) using potentiostatic conditions at various overpotentials. In all cases silver deposited as separate grains, but hollows inside them were not reported.

3.2. Thiourea

Thiourea is applied in many hydrometallurgical procceses, eg.: leaching of noble metals (gold, silver) or as a brightener of cathodic deposits. It is known from literature data that thiourea hinder the dendrites growth. Lacconi and Macagno [3] observed that silver deposited from AgNO$_3$ + 0.5 M HClO$_4$ solution formed separated spherical nodules. It seemed to be advantageous regarding to the aim of our investigations. However, these studies were carried out in dilute solutions (10^{-3} M AgNO$_3$, 10^{-3}–10^{-2} M thiourea), and for high Ag$^+$ concentrations in the bath the conditions changed drastically. Preparation of the solution with 130 g/dm^3 Ag$^+$ and thiourea (10 g/dm^3) became impossible, since in this case Ag$_2$S precipitated ($L_{Ag_2S} = 5.7 \cdot 10^{-51}$). This fact is confirmed by the Pourbaix's diagrams for Ag-CS(NH$_2$)$_2$-H$_2$O system showed in Fig. 2 [10].
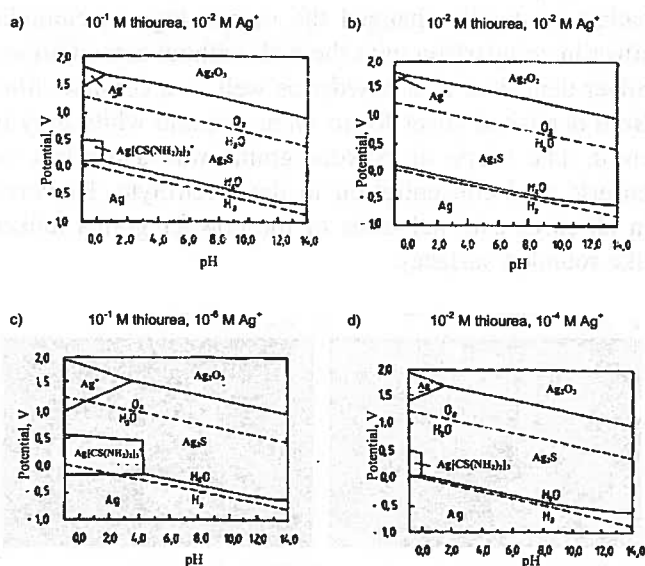

Fig. 2. The E-pH diagrams for Ag-CS(NH$_2$)$_2$-H$_2$O system [10]

The E-pH diagrams indicate that soluble complex of thiourea with silver ions can exists only in acidic solutions. Low Ag$^+$ concentrations in the solution are required for Ag[(CS(NH$_2$)$_2$]$_3$$^+$ formation. At constant thiourea concentration, stability area of Ag[(CS(NH$_2$)$_2$]$_3$$^+$ decreases with increasing Ag$^+$ concentration (compare Figs. 2: a and c or b and d). It is worth noting that Ag$^+$ complexing proceeds only for thiourea concentration at least one order of magnitude

higher than that for silver ions. In an opposite case, silver sulfide precipitates.

In the industrial electrorefining process, the silver ions concentration in the electrolyte is high (more than 1 M). Therefore, at least 760 g/dm^3 thiourea (10 M) must be added to the strong acidified bath to prevent silver sulfide precipitation. However, so high concentration of organic additive would enhance its embedding in the deposit and would decrease the anodic current efficiency (due to thiourea oxidation at the anode). There was no certainty that high concentrations of thiourea could assure $Ag[(CS(NH_2)_2]_3^+$ formation. Moreover, from the viewpoint of industrial practice, too strong acidification of the electrolyte with HNO_3 would decrease the cathodic current efficiency due to the simultaneous reduction of nitrate ions [11]. For these reasons thiourea was eliminated as a potential agent used for the modification of silver morphology during the electrorefining process.

3.3. Tartaric acid

The addition of tartaric acid to the electrolyte containing high concentration of silver ions did not cause any problems with the bath stability. No precipitates were found in the solution even after longer period of storage time.

The presence of tartaric acid in the bath ("TA" baths) drastically changed the morphology of cathodic silver in comparison with the bath without any additives. Silver deposited as a powder as well as a compact film. Both deposited silver forms were mat and white-grey in color. The shape of powder grains was dependent on tartaric acid concentration in the electrolyte. However, in all cases external faces of the powder grains looked like rounded surfaces.
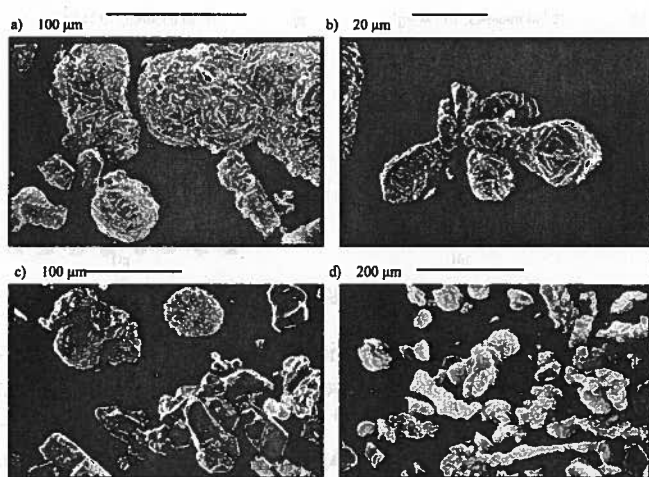

Fig. 3. The morphology of the silver powder deposited from the bath with 2.2 g/dm^3 tartaric acid

Conglomerates of crystallites obtained in the bath with the highest concentration of the additive (2.2 g/dm^3)

consisted of small balls (Fig. 3a) or elongated spherulites (Fig. 3b). Some polyhedrons were also observed (Fig. 3c). The surface of the grains was well developed and characterized with special surface structure. A lot of the grains had irregular shapes (Fig. 3d) and formed porous spatial structures. Typical dendrites were not observed. The grains sizes varied from a few to 200 μm.
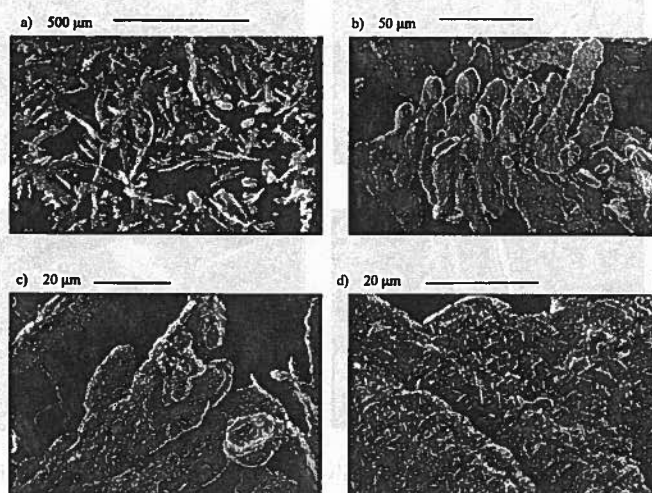

Fig. 4. The morphology of the silver powder deposited from the bath with 1.1 g/dm^3 tartaric acid
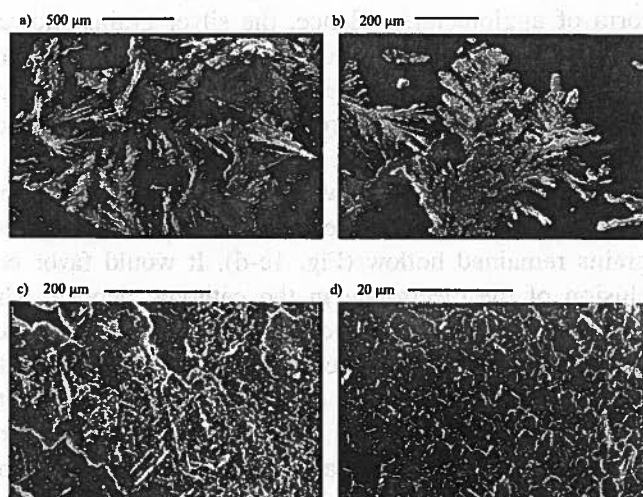

Fig. 5. The morphology of the silver powder deposited from the bath with 0.6 g/dm^3 tartaric acid

When the acid concentration was decreased twice (1.1 g/dm^3) the formation of small "needle" shaped grains with uniform macroscopic sizes was observed. Silver grains consisted of branched and strongly flattened dendrites with rounded edges (Fig. 4a-b). The ball-shaped and polyhedrons crystallites were not found. The surface of the grains was well developed and rough.

At large magnifications distinct "needles" or spherical growths on the grain surface were visible (Fig. 4c-d).

With further decrease of the acid concentration (0.6 g/dm^3) silver deposited as the loose flakes with uniform dimensions. The microscopic observations revealed that the grains were like flat and pinnate leaves (Fig. 5a-b). Their surface was covered with fine spherical or "needle" growths (Fig. 5c-d).

Quantity of deposited silver powder was dependent on the tartaric acid concentration in the bath. With increasing of additive concentration, fraction of the powder decreased and silver showed tendency to deposition as compact film (Fig. 6). For example, at TA concentration of 0.6 g/dm^3 the powder fraction was only about 32% (wt.) of the total cathodic deposit.
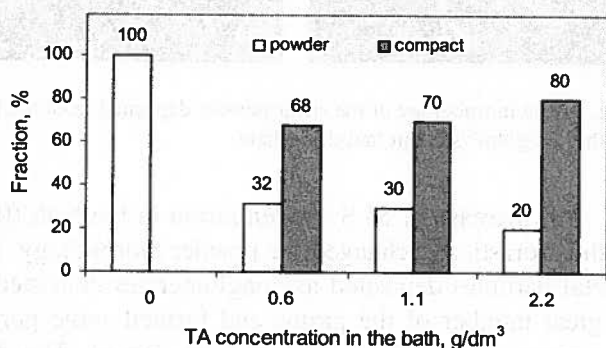

Fig. 6. The influence of the tartaric acid concentration on the fractions of the powder and compact silver deposits

P a p a n a s t a s i o u et al. [4] studied morphology of silver deposited (at 200 A/m^2) from nitrate bath (0.05–0.2 M Ag$^+$) with 0.015 M (2.2 g/dm^3) tartaric acid added. They showed that TA acted as the growth inhibitor and compact silver films were obtained. However, at more diluted solutions deposits were less adherent. Moreover, morphology of deposit surface was governed by the presence of Ag(HA) complex, which concentration depended on the amount of monovalent HA$^-$ anions formed in the first stage of TA dissociation. The same Ag$^+$ concentrations in the bath of the greater HA$^-$ concentrations (influenced by pH) corresponded to smoother deposits. Such tendency was also observed at constant pH: with increasing TA concentration, HA$^-$ concentration also increased and a fraction of compact silver was getting higher. It is worth noting that differences in the form of silver (powder, compact film) resulted from the current density applied at low HA$^-$ concentrations in the baths: the compact film with high roughness was formed at low current density and low Ag$^+$ concentration (200 A/dm^2, ~0.2 M Ag$^+$), the silver powder was formed at high current density and high Ag$^+$ concentration (1050 A/m^2, ~1 M Ag$^+$).

The contents of copper and lead in both fractions of the cathodic silver were determined. It was observed

that the degree of contamination of the deposit depended on the form of silver (Fig. 7). The powder showed more tendency to accumulation of copper and lead than compact silver. Increasing of tartaric acid concentration in the bath was accompanied with increasing amount of the copper and lead in the powder, however, the copper content was about 10–20 ppm higher than that of lead. The copper and lead content in silver increased, respectively: from 20 ppm and 8 ppm (bath without additives) to 107 ppm and 80 ppm (at 2.2 g/dm^3 tartaric acid in the bath). It seemed that such increase of silver contamination resulted from the substantial changes in powder morphology. The same dependence was observed for compact film (36–64 ppm Cu and 16–38 ppm Pb). The tests showed that adsorption of Pb^{2+} ions on the silver was a little higher for powder deposited from the bath with 1,1 g/dm^3 TA addition than from the bath with no additives (0,15 ppm and 7 ppm Pb for concentrations 0,05 g/dm^3 and 0,5 g/dm^3, respectively). The changes in Cu^{2+} adsorption was not observed.
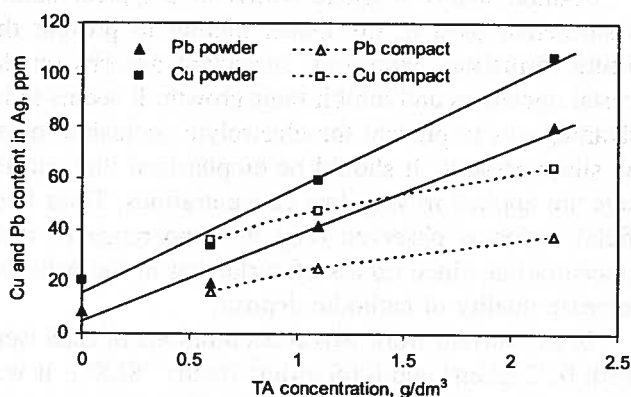

Fig. 7. The influence of the tartaric acid concentration on the copper and lead contents in the powder and compact deposit of silver
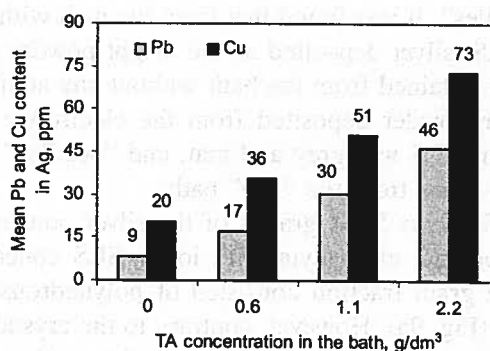

Fig. 8. The influence of the tartaric acid concentration on the copper and lead mean contents in the cathodic silver

The distribution of both silver fractions and their composition allowed calculation of average copper and lead amounts in the cathodic silver. Fig. 8 shows the dependence of the mean content of impurties in the sil-

ver on the additive concentration in the solution. It is seen that the presence of tartaric acid in the bath favored silver contamination with copper and lead. Thus, with increasing acid concentration in the bath, the silver contamination also increased (from 8 ppm to 46 ppm Pb and from 20 ppm to 73 ppm Cu). This fact is disadvantageous from the viewpoint of the silver electrorefining.

The cathodic current efficiency at TA addition reached 100.2%, independently on the additive concentration. It seemed that this additive could be build into the deposit as it is known from the literature [4].

Obtained results showed that tartaric acid did not satisfy the requirements of its usability in the silver electrorefining. This additive favored the compact film deposition and silver contamination.

3.4. Sodium lauryl sulphate

Sodium lauryl sulphate (SLS) is a typical anionic surfactant used in the nickel plating to prevent the pitting formation. Moreover, surfactant adsorbs on the crystal nucleuses and inhibit their growth. It seems to be advantageous to prevent the electrolyte occlusion inside the silver crystals. It should be emphasized that surfactants are applied in very low concentrations. Their beneficial action is observed only in some range of their concentration, since excess of surfactant in the bath can decrease quality of cathodic deposit.

In the current work two concentrations of SLS were used: 0.02 g/dm^3 and 0.08 g/dm^3 (baths "SLS"). It was observed that this additive did not influence in a special way on the form of the deposit and silver deposited as a powder poorly adhered to the substrate. Two fraction of the powder were formed on the cathode: small crystals and "needles". It was found that from the bath with 0.02 g/dm^3 SLS, silver deposited as the bright powder similar to that obtained from the bath without any additives. The silver powder deposited from the electrolyte with 0.08 g/dm^3 SLS was grey and mat, and "needles" were finer than those from the "NO" bath.

Fig. 9 shows SEM graphs of the silver powder obtained from the electrolyte with lower SLS concentration. Fine grain fraction consisted of polyhedrons with flat faces (Fig. 9a). However, contrary to the crystals deposited from the electrolyte without additives, the grains were not elongated but rather oval. Most of the grains were separated, but some conglomerates of crystals were also found (Fig. 9b). Their sizes varied: from 15 μm to 200 μm. Some long dendrites (Fig. 9c) with coarse grained branches (Fig. 9d) were also present in the powder. It was difficult to determine if the silver grains were monolithic ones. However, some small holes were visible

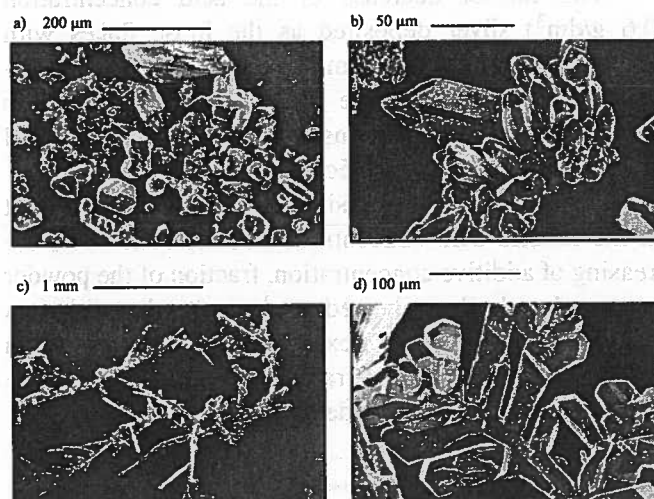on their surface. It suggested that the electrolyte could occlude inside the grains.

Fig. 9. The morphology of the silver powder deposited from the bath with 0.02 g/dm^3 sodium lauryl sulphate

An increase of SLS concentration in the bath (0.08 g/dm^3) drastically changed the powder morphology. The metal particles deposited as conglomerates consisted of a great number of the grains and formed some porous structures with 200 μm in size (Fig. 10a-b). The dendrites showed characteristic branched shapes with rough surface (Fig. 10c-d).
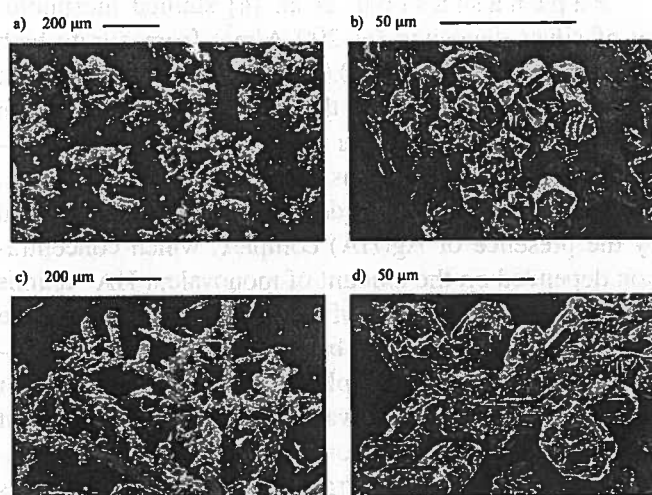

Fig. 10. The morphology of the silver powder deposited from the bath with 0.08 g/dm^3 sodium lauryl sulphate

Modifications of the powder morphology led to the changes in the copper and lead content in the silver. Fig. 11 shows the dependence of the deposit composition on the SLS concentration in the bath. It is seen that both contaminating metals showed different behavior. The increase of the additive content in the solution slightly

decreased lead content in the silver. These variations reached only 5 ppm in comparison with the composition of powder deposited from the bath without any additives. The small amounts of SLS (0.02 g/dm^3) decreased the copper concentration in silver from 20 ppm to 16 ppm. In this case the cathodic powder seemed to be more monolithic than for pure electrolyte and it precluded occlusion of the electrolyte to a certain degree (Figs. 9 and 1). The volume of the occluded electrolyte was estimated as $6 \cdot 10^{-4}$ cm^3/g Ag. With further increase of SLS concentration, copper content in the powder increased (to 45 ppm). This seemed to be favored by the porous structure of the silver deposit and the electrolyte occlusion or metals ions adsorption on the silver surface. This is mainly visible for copper since its concentration in the electrolyte is high.
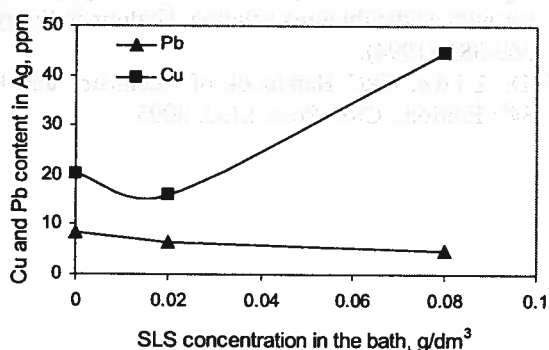

Fig. 11. The influence of the SLS concentration on the copper and lead contents in the cathodic silver

Comparison of silver morphology with Cu and Pb content in the deposit and in the bath suggests that there are two independent processes of silver contamination: the electrolyte occlusion inside the regular silver crystallites (electrolyte without and with 0,02 g/dm^3 SLS) as well as building up Cu^{2+} and Pb^{2+} ions adsorbed on well developed silver surface (electrolyte with 0,08 g/dm^3 SLS). Both mechanisms run parallel, but their participations depends on the SLS concentration in the bath. At present, it is impossible to estimate, which process is predominant. There is no information in literature data about metal ions adsorption on metallic silver powder.

SLS presence increased the cathodic current efficiency from 99.3% to 100.6%. It seems that small amount of the electrolyte was occluded inside the cathodic deposit. This was confirmed by the amount of the contaminations in silver deposited from the solution with 0.08 g/dm^3 SLS.

The changes in the surface tension of the electrolyte, resulting from the surfactant presence, affected also the dissolution of the silver anodes. The anodes after the dissolution in the electrolyte without additives were silver and bright, with sharply outlined metal grains on

the electrode surface. In the electrolyte with low SLS concentration, the anode surface was white and mat, but grain boundaries were clearly visible. The surface of the anodes after dissolution in the bath with 0.08 g/dm^3 SLS was grey, mat, rough and covered with very fine slime. These confirmed the changes of structure observed for the cathodic deposit.

4. Conclusions

Silver deposited from the nitrate bath doped with Cu^{2+} and Pb^{2+} ions as bright powder poorly adhered to the substrate. The powder was characterized with the hollow grains. It favored occlusion of the electrolyte inside grains and contamination of the cathodic deposit with copper and lead.

It was not possible to apply thiourea for the modification of the cathodic silver morphology, since silver sulphide precipitates at high silver ions concentration in the bath

Addition of tartaric acid drastically changed the morphology of the cathodic silver. Silver deposited both, as compact metal and as a powder. The morphology of a powder depended strongly on the additive concentration in the bath. The changes in the silver structure did not decrease copper and lead contents in the deposit. An increase of the acid concentration favored contamination of the deposit.

Sodium lauryl sulphate changed slightly morphology of powder, however it was beneficial only at low concentration. Under these conditions silver deposited as a coarse grained powder with lower copper and lead content than that obtained from the bath without any additives.

Silver contamination with copper and lead depends on the morphology of the cathodic deposit. There are two probable mechanisms of imputries incorporation: occlusion of the electrolyte inside of grains with regular shapes and building up of the metal ions adsorbed on well developed silver surface.

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